Growth and Surface Structure of Ferroelectric Thin Films

J. A. Eastman†, G. B. Stephenson†, S. K. Streiffer†, A. Munkholm†, Carol Thompson§,†, D. D. Fong†, M. V. R. Murty†, M. E. M. Aanerud§, O. Auciello†, G.-R. Bai†, and L. Thompson†

†Materials Science Division, Argonne National Laboratory, §Department of Physics, Northern Illinois University

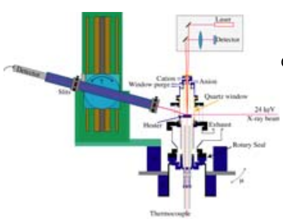
Summary

We have constructed an MOCVD system on BESSRC beamline 12-ID-D of the Advanced Photon Source, for *in-situ* studies of ferroelectric thin films using grazing incidence, real-time x-ray scattering. The precisely controlled environmental conditions available in this system allow careful investigation of growth behavior, surface reconstructions, phase transition behavior, and stress relaxation, among other reversible and irreversible phenomena. Epitaxial single crystal $PbTiO_3$ films are deposited on $SrTiO_3$ substrates, using tetraethyl lead, titanium isopropoxide, and O_2 as precursors. Experiments being performed include characterization of the effect of process parameters on the microstructure of the growing film, and of the surface structure of $PbTiO_3$ in equilibrium with PbO vapor. This surface structure is found to be a single antiferrodistortive layer with c(2x2) symmetry.

Motivation

- Wish to understand and control synthesis of complex oxides at the same level that is currently achieved with semiconductors.
- $PbTiO_3$ is a model perovskite – it is the prototype of a wide class of ferroelectric materials, and is well-characterized and exhibits "benchmark" phase transformation behavior.
- High quality $PbTiO_3$ thin films are produced by metalorganic chemical vapor deposition (MOCVD).
- The atomic-scale growth mechanisms and surface structures in the MOCVD environment have yet to be observed.

System on BESSRC Beamline 12-ID-D, APS

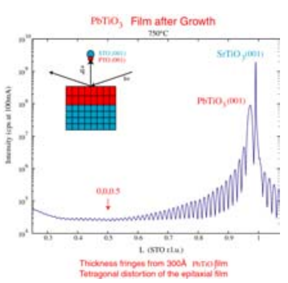


Scattering Methodology
Grazing incidence scattering for surface sensitivity
Good time resolution (sub-second)

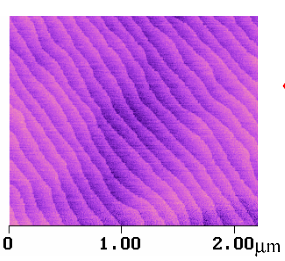
G.B. Stephenson, et al., *MRS Bull.* **24** (1) 21 (1999)

Substrate temperature	600-850°C	
Reactor pressure	10 Torr	
OM precursor temperature	$Pb(C_2H_5)_4$ $Ti(OC_3H_7)_4$	-12-21 °C 29-30 °C
Precursor pressures	$Pb(C_2H_5)_4$ $Ti(OC_3H_7)_4$	50-800 Torr 90 Torr
Precursor flow	$Pb(C_2H_5)_4$ $Ti(OC_3H_7)_4$	2-100 sccm 2-100 sccm
Flow rate of reactant gas (O_2)	375 sccm	
Total flow rate	1710 sccm	
Substrates	$SrTiO_3(001)$, $SrRuO_3/SrTiO_3(001)$	

Film Microstructure



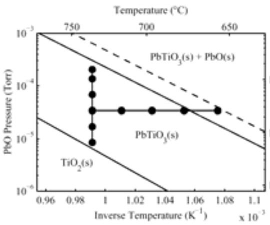
- Typical symmetric x-ray scattering pattern from a $PbTiO_3$ film grown in our system.



- Scanning probe microscopy image of a $PbTiO_3$ film grown in our system. Steps separating terraces are a single unit cell in height.

The Stable Process Window

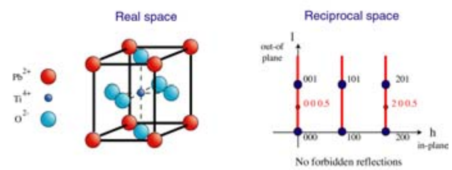
- A stable growth window exists with respect to PbO pressure (controlled by input of tetraethyl lead into the MOCVD system), were $PbTiO_3$ is the stable phase and excess PbO volatilizes. (See for example G. Dormans, et al., J. Cryst. Growth **123**, 537 (1992).)
- Circles indicate typical growth conditions explored for our system.



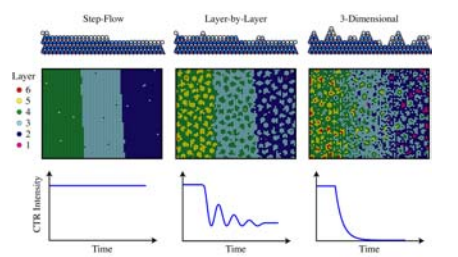
Phase boundaries calculated from I. Barin, Thermochemical Data of Pure Substances, 3rd Edn., VCH, New York, 1995.

Tracking Surface Evolution During Growth

- Truncation of crystal at surface causes streaks of intensity to extend away from Bragg peaks, perpendicular to the surface.



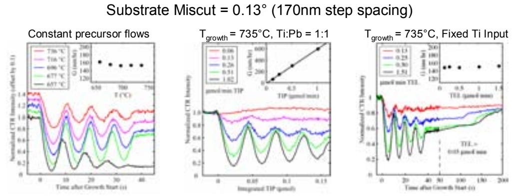
- Evolution of surface during growth tracked via the evolution of the crystal truncation rods (CTRs), typically at the 2 0 1/2 position.



- Step-flow growth: CTR intensity is constant, as surface morphology is constant.
- Layer-by-layer growth: CTR intensity oscillates as individual monolayers nucleate and coalesce.
- Three-dimensional growth: CTR intensity decays as surface roughens.

Growth Mode vs. Temperature, Growth Rate, and PbO Pressure

Substrate Miscut = 0.13° (170nm step spacing)

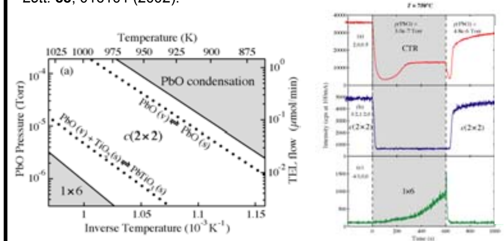


- Strong tendency for $PbTiO_3$ to grow in layer-by-layer mode.
- Transition to step-flow growth observed as growth rate is reduced. First demonstration of step-flow growth for MOCVD of a perovskite.
- With lower TEL inputs, growth tends towards step-flow and surface recovers more quickly after growth.
- Surface mobility increases with decreasing PbO partial pressure.

M.V. Ramana Murty, S.K. Streiffer, G.B. Stephenson, J.A. Eastman, G.R. Bai, A. Munkholm, O. Auciello, and Carol Thompson, *Appl. Phys. Lett.* **80**, 1809 (2002).

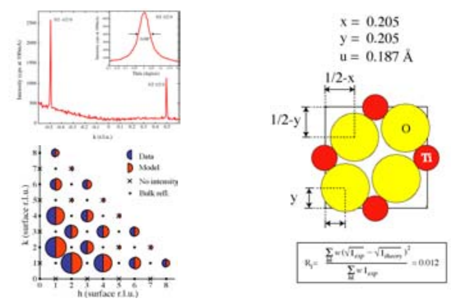
$PbTiO_3$ Surface Structure

A. Munkholm, S.K. Streiffer, M.V. Ramana Murty, J.A. Eastman, Carol Thompson, O. Auciello, J.F. Moore, and G.B. Stephenson, *Phys. Rev. Lett.* **88**, 016101 (2002).

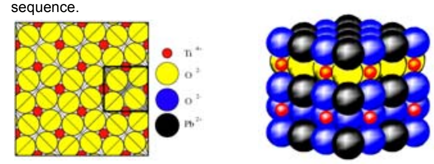


- Find that a c(2×2) reconstruction (or, equivalently, ($\sqrt{2}\times\sqrt{2}$) R45° with respect to the underlying $PbTiO_3$ unit cell) is the equilibrium surface structure across the entire $PbTiO_3$ single-phase field.
- A poorly ordered (1×6) reconstruction evolves when PbO pressure falls below the $PbTiO_3$ stability line, and is believed to be a nonequilibrium Ti-rich structure.

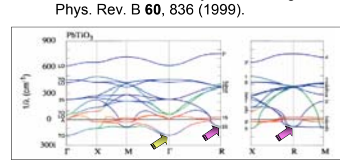
Structural Model for Equilibrium $PbTiO_3$ ($\sqrt{2}\times\sqrt{2}$) R45° Reconstruction



- The equilibrium surface is a PbO terminated single-unit-cell layer with an antiferrodistortive structure, obtained by oxygen octahedral rotations. L-scans (not shown) confirm the out-of-plane layer sequence.



- Competing zone-center (yellow arrow) and zone-boundary (purple arrows) distortional modes have been identified by *ab-initio* calculations
  - W. Zhong and D. Vanderbilt, Phys. Rev. Lett. **74**, 2587 (1995).
  - Ph. Ghosez, E. Cockayne, U.V. Waghmare, and K.M. Rabe, Phys. Rev. B **60**, 836 (1999).



Phonon modes calculated using density functional perturbation theory, by Ghosez, et al.

- Postulate that there is stabilization of the suppressed zone-boundary antiferrodistortive mode by the surface.

Conclusions and Future Work

- Growth modes mapped for $PbTiO_3$. Layer-by-layer and step-flow modes achieved.
- Higher surface mobilities occur at lower PbO overpressures.
- Surface structures identified as a function of thermodynamic activity.
  - Surface structure in equilibrium with PbO consists of an antiferrodistortive mode, similar to that found in $SrTiO_3$ at low temperatures.
  - Connection to energetics of the ferroelectric transition energy scale.
- Add additional composition capabilities: Zr in near term; Nb, Mg in long term.
- Explore growth of superlattice structures: Atomic Layer Epitaxy.

BES - DOE

This work was supported by the U. S. Department of Energy, Basic Energy Sciences, under contract W-31-109-ENG-38, and by the State of Illinois under HECA.

MSD - ANL